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Reinvestigation thermoelectric properties of CuAlO₂

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Abstract

Bulk CuAlO₂ delafossite has been synthesized by solid state reaction to reinvestigate the thermoelectric properties. The electrical conductivity, Seebeck coefficient and thermal conductivity were measured in a high temperature range of 300 to 960 K. The result of positive sign of Seebeck coefficient confirms p-type nature of CuAlO₂ compound. The results of bulk sample for Seebeck coefficient, the electrical conductivity and thermal conductivity are range of 900 to 300 μ V/K, of 0.01 to 2 S/cm, and of 3.5 W/mK to 1.5 W/mK. The maximum ZT value of bulk sample is 0.017 at a 960 K. These results can be concluded that the bulk CuAlO₂ by solid state displays thermoelectric material.

Keywords: Thermoelectric. ; CuAlO₂. ; Delafossite oxide. ; Seebeck coefficient. ; Dimensionless Figure of Merit.

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1. Introduction

The thermoelectric phenomenon [1-2] is mentioned to effect in materials which can generate electricity from heat and can converse electricity to temperature gradient. The thermoelectric generator can apply to electric energy source in satellite, watch, car, etc. The reverse effect as thermoelectric coolers can apply for refrigerators and cooling systems such example as: CPU cooling, can cooler, vaccine cooling etc. The performance of the thermoelectric material is determined by the dimensionless Figure of Merit, $ZT = (\sigma S^2 / \kappa) T$, where S is the Seebeck coefficient, σ and κ are the electrical, thermal conductivity, and T is the absolute temperature, respectively. High ZT value of materials occur in large S and σ , while low κ values.

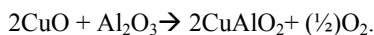
Recently, delafossite compound has been growth interest for thermoelectric materials [3]. The delafossite are classified in a group of ternary oxides whose general chemical formula is $A^+B^3+O_2$ [3]. The compounds in a delafossite group consist of $CuFeO_2$, $CuAlO_2$, $CuCoO_2$, $PtCoO_2$ and $PdCoO_2$ etc. [4-7]. Especially, $CuAlO_2$ compound illustrates high performance for thermoelectric materials. Kawazoe et al. [8] have reported the film electrical conductivity of 1 S/cm and Park et al. [9] have reported the electrical conductivity of bulk in a range of 1 to 2 S/cm. Park et al. [9] and Liu et al. [10] have showed that the temperature independence of thermoelectric properties of $CuAlO_2$ for Seebeck coefficient, thermal conductivity, Power Factor and ZT are around 500 $\mu V/K$, 0.2 W/cmK, 4×10^{-5} W/mK², and 0.0045, respectively, at high temperature. The $CuAlO_2$ compound belongs to a delafossite group of ternary oxides whose chemical formula is $A^+B^3+O_2$ [11-13]. Its structure is formed by 2-D layers of the Cu^+ cations and the AlO_6 octahedral-shaped layers which are alternatively stacking along the c-axis. The Cu^+ cation is bonded with two O^{2-} anions forming dumbbell-shaped [O-Cu-O] structure in the c-axis. The AlO_6 octahedral structure is formed by sharing the $[AlO_2]^-$ edges. The trivalent Al^{3+} cation occupies the middle position of the distorted octahedral block with surrounding six O^- ions containing six linking bonds of Al-O.

Moreover, there are many reports showing experimental data of bulk [11] and film [1, 12] of the $CuAlO_2$ compounds exhibiting p-type nature. Liu et al. [17] have showed that the temperature independence of thermoelectric properties for Seebeck coefficient, thermal conductivity, Power Factor and Dimensionless Figure of Merit are around 500 $\mu V/K$, 0.2 W/cmK, 4×10^{-5} W/mK², and 0.0045, respectively, at high temperature.

The aim of this paper is to reinvestigate the temperature dependence of thermoelectric properties of the bulk $CuAlO_2$ compound by solid state reaction method with comparison to previous reported. The temperature dependences of the thermoelectric properties of bulk $CuAlO_2$ were investigated. In addition, the x-ray diffraction (XRD), electrical conductivity, Seebeck coefficient, thermal conductivity, thermoelectric properties, and TGA weight loss were performed and discussed.

2. Materials and Methods

Bulk $CuAlO_2$ polycrystalline sample was synthesized by a conventional direct solid-state reaction according to the following equation:



The starting materials of stoichiometric amounts of high-purity powders of CuO (Merk, 99.98%) and Al_2O_3 (Sigma-Aldrich, Inc., 99%) were sufficiently mixed and ground in an agate mortar to ensure homogeneity. After a homogenous mixture was obtained, the mixture was cool pressed into pellet of 12 mm diameter with 2.5 mm thickness by hydraulic pressure of 3 Mpa. The obtained pellet was sintered by performing inside an alumina boat in a furnace at 1050 °C in air for 20 h. After heat treatment, the sample was rapidly quenched to room temperature.

The crystallography of samples was determined by a powder X-ray diffraction (XRD) using PHILIPS model: X' Pert MPD analysis using $Cu K\alpha$ radiation with $2\theta = 10^\circ - 80^\circ$ with 0.02 steps. The lattice parameters were determined by a Rietveld refinement program, X'Pert High Score Plus V2.0a. Microstructure of the sample was observed by scanning electron microscope (SEM) using the JEOL model: JSM-5410. The oxygen content and melting point were analyzed by using thermogravimetric analysis (TGA) by the Perkin Elmer TGA7 under N_2 atmosphere with scanning step of 10.00 C/min in alumina crucible. The Seebeck coefficient and electrical resistivity

were simultaneously measured on the $4.63 \times 3.52 \times 19.22 \text{ mm}^3$ sample bar using an ULVAC-RIKO ZEM-3 thermoelectric property measurement system under a low-pressure helium atmosphere. The thermal conductivity was determined from thermal diffusivity and specific heat on pellets of 12 mm diameter with thickness of 1.6 mm by using the ULVAC SINKU RIKO Inc. model: TC-7000 laser-flash method.

3. Results and Discussion

3.1 Characterization

An XRD pattern of the CuAlO_2 sample is shown in Fig. 1. The pattern exhibits peaks of hexagonal delafossite-type structure having space group: $R\bar{3}m(166)$ corresponding to the standard JCPDS#35-1401. The lattice constants of CuAlO_2 are 2.852 Å and 16.954 Å for a-axis and c-axis, respectively. This result agrees with the standard JCPDS#35-1401 and relates to the computational results by method of the plane-wave pseudo-potential based on density functional theory (DFT) [14] with $a = 2.802 \text{ Å}$ and $c = 16.704 \text{ Å}$ for a-axis and c-axis, respectively.

Energy dispersive X-ray spectroscopy (EDS) result showing a SEM image and inserted chemical compositions of the CuAlO_2 sample are shown in Fig.2. The plan view of SEM image displays the morphology of sample. The SEM shows that the microstructure of crystal grain size is larger than 10 µm. The EDS result confirms the chemical compositions of the sample.

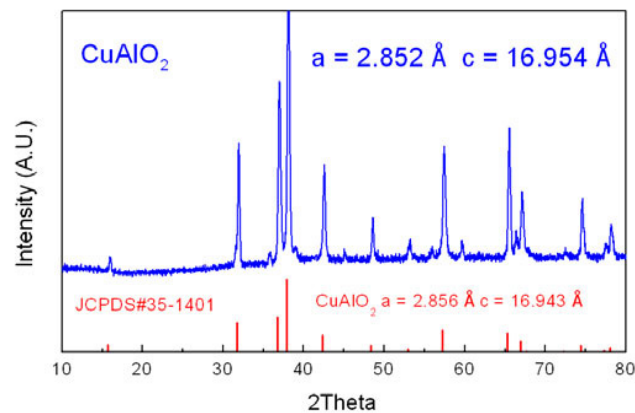


Fig. 1. The XRD pattern of the CuAlO_2 sample compared with JCPDS data.

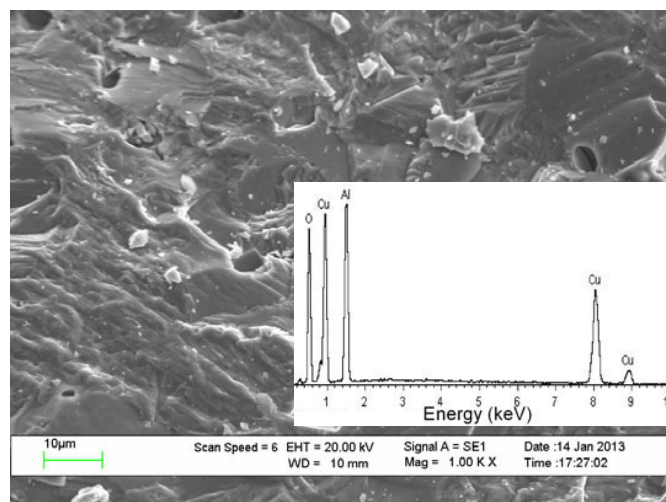


Fig. 2. The energy dispersive X-ray spectroscopy and the microstructure of the CuAlO₂ pellet sample.

The thermogravimetric analysis (TGA) and differential thermal gravimetric (DTG) results of the CuAlO₂ sample are shown in **Fig. 3**. The information of weight loss is used to determine the oxygen insertion into the structure [15-16]. The CuAlO₂delafossite allows oxygen to exist in the center lattice position of the Cu⁺ triangles in the Cu⁺ layers. The excess oxygen influences hole carrier concentration in the compound. Also, this defect plays an important role to display p-type conductor within the CuAlO₂. The metal deficient oxide can be displayed by the nonstoichiometric defect relation [17] as following: $O_2(g) = 2O_O^X + V_{Cu}^- + V_{Al}^{3-} + 4h^+$, where O_O , V_{Cu} , V_{Al} and h represent the original lattice sites of oxygen, Cu vacancy, Al vacancy and hole, respectively. The superscripts X, - and + are the effective neutral, negative and positive charge states, respectively. The results as in **Fig 3** show that the starting weight loss peak and the abrupt ending weight loss peak for oxygen de-intercalation process occur at about 700 °C and 800 °C, respectively. This is the total weight loss as 0.5%. The excess oxygen contributes to the non-stoichiometry formula of the CuAlO₂delafossite as CuAlO_{2+δ} (where δ > 0). The δ for CuAlO₂ structure exhibits δ = 0.005 atom per formula as CuAlO_{2+0.005} per formula. The abrupt weight loss at temperature 1300 °C is the melting point of the CuAlO₂ compound.

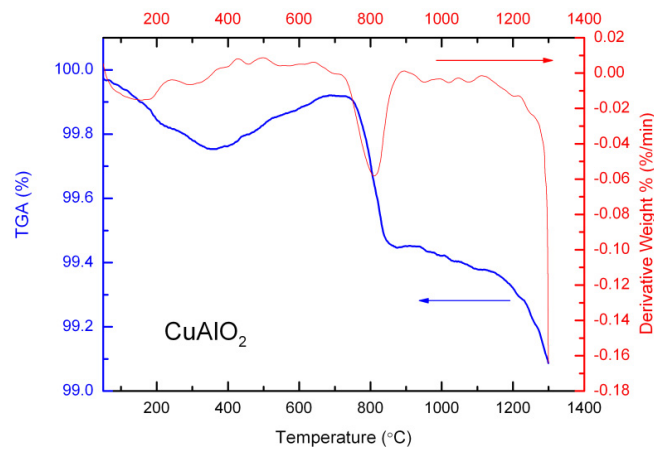


Fig. 3. The TGA and DTG weight loss curves of the CuAlO₂ sample.

3.2 Seebeck coefficient and Electrical conductivity

The Seebeck coefficient (S) of the CuAlO₂ samples as a function of invert temperature is shown in **Fig. 4**. The S values were measured on the bulk sample density of 4.68 g/cm³ that is 91.76% of the theoretical density. The results show that the Seebeck coefficients are positive sign over the measured temperature range indicating p-type conductor behavior due to behavior of hole majority carriers. The results of Seebeck coefficients exhibit values ranging from 900 to 300 μV/K in the temperature range of 300 to 960 K. The Seebeck coefficient tends to rapidly decrease as a result of the increasing temperature.

The comparison of our S results to other previous works with displaying in invert temperature is shown in **Fig. 4**. The S results are compared to the previous reports by Park et. al. [18] for the sample density of 3.741 g/cm³ (73%) by sintering at 1433 K and density of 3.818 g/cm³ (74%) by sintering at 1473 K, by Dura et. al. [19] for the sample density of 4.96 g/cm³ (97%) of the Micro crystal size sample and 4.43 g/cm³ (87%) of the Nano crystal size sample, and by Liu et. al. [17] for the sample density of 95.9%. The results display that our finding of the S at high temperature is close to the results of Dura's sample of the Nano sample (87%), of Park's sample for both sintering at 1433 K (73%) and at 1473 K (74%). At temperature of 300 K, the S of our sample are close to the S of Dura of the Micro sample (97%). The S of our data are similar to the S of Liu (95.9%) for invert temperature range 1.5 to 2.5. The results indicate that our result is higher than that results of Dura of the Nano sample (87%), and of Park for both sintering at 1433 K (73%) and 1473 K (74%). In addition, our result is lower than those results of Dura of the Micro

sample (97%) and of Liu et al.'s (95.9%). Obviously, the results imply that S is strongly dependent of the density of sample. Therefore, the S value of CuAlO_2 can be improved by selecting in high density sample.

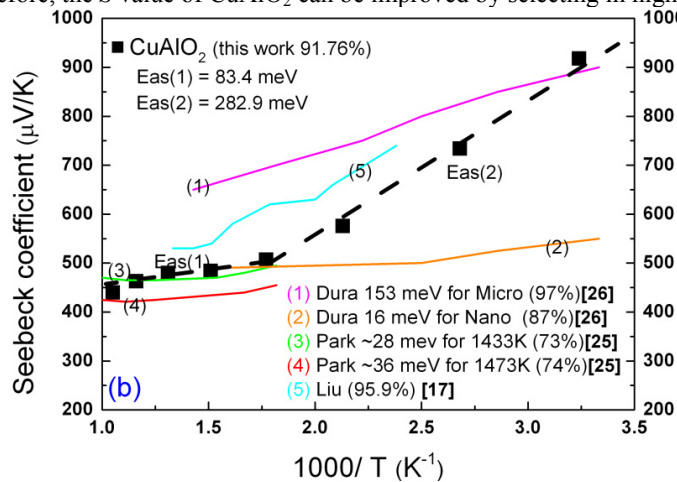


Fig. 4. The temperature dependence of Seebeck coefficient with previous reports.

The temperature dependence of the electrical conductivity (σ) of the CuAlO_2 samples is also displayed in Fig. 5. The values of electrical conductivity are measured in the high temperature of 300 to 960 K. The σ exhibit values ranging from 0.01 to 2 S/cm as the temperature ranging from 300 to 960 K. At 900 K, the electrical conductivity displays a high value close to 1 S/cm. Trend of σ is rapidly reduced as a result of the increasing temperature.

The comparison of σ value to the previous works with displaying in invert temperature is shown in Fig. 5. The results display that the σ of our sample (91.76%) is close to the results of Dura [19] of the Micro sample (97%), and Liu [17] (95.9%). The σ value from this study is far from the results of Park [18] of the both samples sintering at 1433 K (73%) and at 1473 K (74%), and of Dura of the Nano sample (87%). For result of all results, the high σ is observed on the sample densities 73% and 74% of Park samples. This implies that high σ values of the CuAlO_2 compound exist on the sample high density from Park's method.

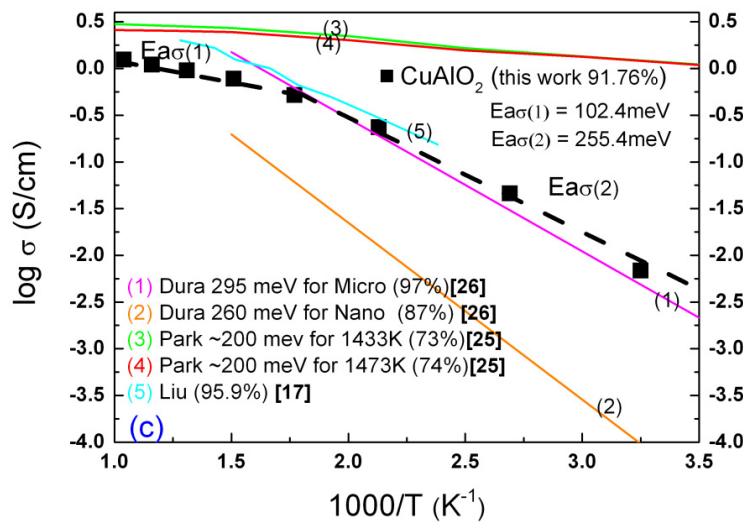


Fig. 5. The curve of $\log \sigma$ vs. $1000/T$ of CuAlO_2 sample with previous reports.

3.3 Thermal conductivity and Dimensionless Figure of Merit (ZT)

The temperature dependence of the thermal conductivity (κ) is shown in **Fig. 6**. The thermal conductivity of the CuAlO₂ samples were measured using a laser flash method with the relation of $\kappa = dC_p a$ [13] where d , C_p and a are the bulk density of sample, heat capacity and thermal diffusivity, respectively. The density of the bulk CuAlO₂ sample is 4.68 g/cm³. The results show that the values of κ are decreased in the range of 3.5 W/mK to 1.5 W/mK with increased temperature. The maximum κ value is 3.5 W/mK at room temperature and the minimum κ value is 1.5 W/mK in the temperature range of 700 K to 960 K. These results exhibit that the thermal conductivity of the CuAlO₂ sample is decreased with increasing temperature.

The comparison of our finding for κ value to previous work is shown in **Fig. 6**. The results show that the κ value of our sample is close to the κ of Dura [19] for the Nano samples with density of 87%. The high values of κ occur in the sample of Liu [17] with high sample density of 95.9%. The lowest of κ values appears on the sample of Dura [19] for Nano sample with low sample density of 87%. This implies that the low value of thermal conductivity of CuAlO₂ sample can occur in the sample of Nano crystal size with low density.

The temperature dependence of the dimensionless Figure of Merit (ZT) for thermoelectric property of our CuAlO₂ sample is also shown in **Fig. 6**. The $ZT (= S^2 \sigma T / \kappa)$ [10] value is computed from the Figure of Merit ($Z = S^2 \sigma / \kappa$) and the temperature (T). The results of ZT are in the ranging of 0.001 to 0.017 with the temperature ranging of 300 to 960 K. The results reveal that the ZT increases with the increasing temperature. In addition, the maximum of ZT value of the CuAlO₂ samples is 0.017 at a high temperature of 960 K.

In comparison of the ZT values to other work, our ZT values are comparable to the results of Liu et. al. [17]. The ZT result of the Liu sample is 0.004 at temperature 750 K for the sample density of 95.9% on sintering by hot press method. At temperature 750 K, our ZT result is 0.009 for the sample density of 91.76 %. The finding reveals that our sample shows higher ZT value than that of the Liu sample. This implies that the high performance for thermoelectric property of CuAlO₂ can be improved by optimization the density for parameters of S , σ and κ .

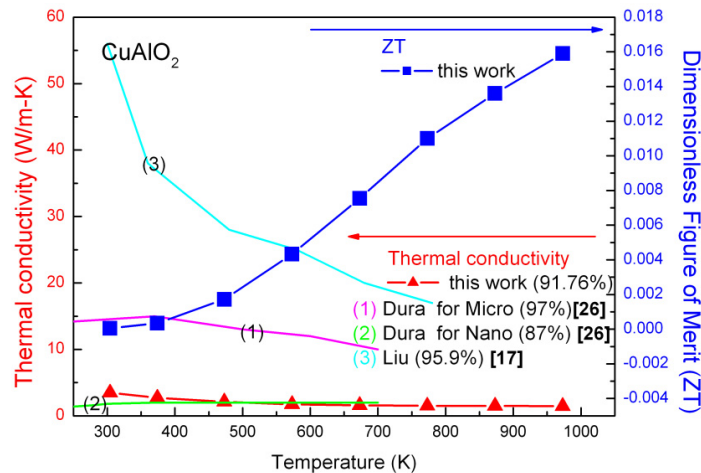


Fig. 6. The temperature dependence of the thermal conductivity and ZT of the CuAlO₂ sample with previous reports.

4. Conclusion

The objective of this study is to reinvestigate thermoelectric properties of bulk CuAlO_2 delafossite compound at high temperature in preparing by solid state reaction method. The bulk sample is obtained density in 91.76%. The electrical conductivity, Seebeck coefficient, and thermoelectric properties were measured at high temperatures ranging from 300 to 960 K. The Seebeck coefficient shows positive sign confirming p-type conductor behavior. The Seebeck coefficient displays from 900 to 300 $\mu\text{V/K}$, the electrical conductivity exhibits from 0.01 to 2 S/cm, and thermal conductivity illustrates in the range of 3.5 W/mK to 1.5 W/mK with the temperature range of 300 to 960 K. The maximum ZT value is 0.017 at a 960 K. Indeed, the bulk CuAlO_2 delafossite oxide compounds sintering by solid state reaction display p-type oxide thermoelectric material.

Acknowledgments

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